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VULCANIZABLE VINYL-CONTAINING ORGANOPOLYSILOXANES AND PROCESS OF PREPARING ELASTOMERS THEREFROM

Dallas T. Hurd, Burnt Hills, and Robert C. Osthoff, Schenectady, N. Y., assignors to General Electric Company, a corporation of New York

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This invention relates to vulcanizable vinyl-containing organopolysiloxanes having carbon black and sulfur incorporated therein, to the process of vulcanizing these vulcanizable materials, and to the resulting vulcanizates. More particularly, this invention is concerned with the vulcanizate from 60 to 94.5 parts by weight organopolysiloxane having the average structural formula

$$(1) \qquad (CH_2{=}CH)_a(R)_bSiO_{\frac{4-(a+b)}{2}}$$

where a has a value of from 0.0086 to 0.18, b has a value from 1.80 to 2.0014 and the sum of $a+b$ is equal to from 1.98 to 2.01, said organopolysiloxane containing from 5 to 40 parts by weight of carbon black and 0.5 to 5 parts by weight of finely divided sulfur. In the above formula R represents organic radicals, at least 50 mole percent of which are methyl with the remainder of the radicals being selected from the class consisting of alkyl radicals, e. g., methyl, ethyl, propyl, butyl, octyl, decyl, octadecyl, etc. radicals; cycloalkyl radicals, e. g., cyclohexyl, cycloheptyl, etc. radicals; aryl radials, e. g., phenyl, diphenyl, naphthyl, etc. radicals; alkaryl radicals, e. g., tolyl, xylyl, ethylphenyl, etc. radicals; aralkyl radicals, e. g., benzyl, phenylethyl, etc. radicals; and halogenated aryl radicals, e. g., chlorophenyl, dibromophenyl, etc. radicals.

In the past, attempts have been made to form carbon black filled organopolysiloxane elastomers by various methods. However, in general, only inferior products have been obtained since the general method of cross-linking organopolysiloxane gums has been with typical free radical polymerization agents such as the acyl peroxides, e. g., benzoyl peroxide, or with azo compounds such as α,α'-azodiisobutyronitrile. In general, these free radical cross-linking agents have been found to be relatively ineffective in polymerizing organopolysiloxane systems containing carbon black, presumably because of some reaction which occurs between the cross-linking agent and the carbon black.

We have now discovered that by forming a highly viscous organopolysiloxane fluid or gum within the scope of Formula 1 which contain silicon bonded vinyl radicals, we are able to incorporate carbon black and sulfur curing agents such as elemental sulfur, sulfur halides, organic sulfides, etc., into the vinyl-containing organopolysiloxane and vulcanize the resulting mixture by heat. The resulting vulcanizates are characterized by their flexibility at temperatures below −50° C., by their outstanding thermal stability at temperatures as high as 150° C., by their high tensile strength and elongation, and by their conducting properties. The vulcanizates are also characterized by their low cost because of use of the relatively inexpensive carbon black filler instead of the more expensive silica aerogel which is usually used in organopolysiloxane elastomers.

The vinyl-containing organopolysiloxane fluids and gums of Formula 1 which may be compounded with carbon black and sulfur and subsequently vulcanized, may be

described as organopolysiloxanes containing an average of from 1.98 to 2.01 organic radicals bonded to silicon through silicon carbon linkages with the remainder of the valences of the silicon atoms being satisfied by silicon-oxygen linkages. Of these silicon bonded organic radicals, from 0.0086 to 0.18 silicon bonded vinyl radicals are present per silicon atom. The fluids and gums within the scope of Formula 1 may be formed in the well known manner by the rearrangement and condensation (polymerization) of lower molecular weight organopolysiloxanes in the presence of a suitable organopolysiloxane polymerization catalyst. The relatively low molecular weight starting materials used for the rearrangement and condensation may comprise any mixture of low molecular weight organopolysiloxanes in which the silicon bonded organic radicals are present in a ratio suitable to give the desired general structure of Formula 1 upon rearrangement and condensation.

The viscous fluids and gums within the scope of Formula 1 may be prepared by copolymerizing a low molecular weight organopolysiloxane containing silicon bonded vinyl radicals with one or more low molecular weight organopolysiloxanes containing only saturated hydrocarbon radicals attached to silicon. The low molecular weight organopolysiloxanes containing silicon bonded vinyl radicals and the method of forming compositions within the scope of Formula 1 are well known. See, for example, Roedel Patent 2,420,911, issued May 20, 1947; Marsden Patent 2,445,794, issued July 27, 1948; and Hurd Patent 2,645,628, issued July 14, 1953. The relatively low molecular weight organopolysiloxane containing a silicon bonded vinyl radical may be prepared, for example, by hydrolyzing a silane containing at least one silicon bonded vinyl radical and at least one silicon bonded hydrolyzable group. Thus, methylvinylsiloxanes may be prepared by hydrolyzing methylvinyldichlorosilane or methylvinyldiethoxysilane with water or aqueous HCl. This hydrolysis results in an aqueous phase and an organopolysiloxane phase containing both linear and cyclic methylvinylsiloxanes of varying chain lengths. After hydrolysis, the organopolysiloxane phase may be distilled to isolate compounds such as 1,3,5-trimethyl - 1,3,5 - trivinylcyclotrisiloxane, 1,3,5,7 - tetramethyl - 1,3,5,7 - tetravinylcyclotetrasiloxane, 1,3,5,7,9-pentamethyl - 1,3,5,7,9 - pentavinylcyclopentasiloxane, 1,3,5,7,9,11 - hexamethyl - 1,3,5,7,9,11 - hexavinylcyclotetrasiloxane, as well as higher cyclic methylvinylsiloxanes and a number of linear methylvinylsiloxanes. Other organopolysiloxanes containing silicon bonded vinyl radicals may be prepared by hydrolyzing silanes such as divinyldichlorosilane, divinyldiethoxysilane, vinyltriethoxysilane, trivinylchlorosilane, etc., and separating the organopolysiloxane phase from the aqueous phase.

The low molecular weight organopolysiloxane containing only saturated hydrocarbon radicals bonded to silicon with which the vinyl-containing organopolysiloxane is copolymerized, may be one or more cyclic organopolysiloxanes having the formula

$$(2) \qquad [(R')_2SiO]_n$$

where n is an integer from 3 to 10 or more and R' represents members selected from the class consisting of alkyl radicals, e. g., methyl, ethyl, propyl, butyl, octyl, decyl, etc. radicals; cycloalkyl radicals, e. g., cyclohexyl, cycloheptyl, etc. radicals; aryl radicals, e. g., phenyl, diphenyl, naphthyl, etc. radicals; alkaryl radicals, e. g., tolyl, xylyl, etc. radicals; aralkyl radicals, e. g., benzyl, phenylethyl, etc. radicals; haloaryl radicals, e. g., chlorophenyl, dibromophenyl, etc. radicals; and mixtures of the aforesaid radicals. Typical compounds within the scope of Formula 3 include, for example, octamethylcyclotetrasiloxane, tetramethyltetraethylcyclotetrasiloxane, octaphenyl-